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Statistics of open multi-component system : probability, chemical equilibrium and stability

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Abstract : The paper deals with the derivation of the probability distribution of an open multi-component system, the condition of chemical equilibrium, the law of mass action and the criteria of chemical stability on the basis of a probabilistic model of the open multi-component system

Keywords : Open multi-component system, statistical model, probability distribution, chemical equilibrium, law of mass action and stability

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1. Introduction

In thermodynamics, the condition of thermodynamic equilibrium and the stability of the equilibrium state is based on some extreme principles or on the extreme values of some thermodynamic potentials. For example, we have the principle of maximum-entropy, the principle of minimum energy or free-energy *etc.* In statistical thermodynamics, Boltzmann entropy is defined to be proportional to the logarithm of the total number of microstates (or complexions) or thermodynamic probability. In statistical thermodynamics, the thermodynamic equilibrium which is obtained by maximising the Boltzmann entropy or equivalently the thermodynamic probability is identified, according to Boltzmann and Planck, to the most-probable state of the system. However, thermodynamic probability is not a probability, it is an integer. So the identification of thermodynamic equilibrium with the most probable state, in the sense of Boltzmann and Planck is not proper, it leads to some confusions [1].

The object of the present paper is to remove this misconception by introducing probability proper by for the macroscopic state of a multi-component system and defining thermodynamic equilibrium as the state obtained by maximising the probability subject to the given constraints. As an application, we have derived the condition of chemical equilibrium, the law of mass action and the condition of chemical stability of the multi-component system.

2. Multi-component system : statistical model and probability distribution

Let us consider an open multi-component system comprising of n chemically reacting components (substances or species). Let N_i (i = 1, 2,....,n) be the number of molecules of the i-th component. The system is assumed to be at uniform temperature T and constant volume V. It is assumed that the reactions proceed sufficiently slowly as not to disturb seriously the equilibrium energy distribution of each component to any appreciable extent [2]. We also assume ideal gas (or mixture) model of the system obeying classical statistics.

The microscopic state of the system at any time t is given by the set of the molecules $A_n = \{N_1, N_2, ...N_n\}$. In view of the many-body aspect of the system, the molecular numbers $\{N_1, N_2, ... N_n\}$ are assumed to be random variables and we are to find out the probability distribution of N_i (i = 1, 2, ...n). Let $P(N_i)$ be the probability distribution

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of N_i (i = 1, 2, ...n). Then the entropy of the i-th component (or species) is given by the generalised Boltzmann-Gibbs entropy [3]

$$S_i(P/m) = -\sum P(N_i)\ln\frac{P(N_i)}{W(N_i)} \tag{2.1}$$

where the summation is over all possible values of N_i, $W(N_i)$ is some measurable function of Ni defined on N_i – space and constitutes the prior information about N_i. This measure, according to classical statistics, is given by [4,5].

$$W(N_i) = 1/N_i!. \tag{2.2}$$

The main problem of the statistical model is to estimate the probability distribution $P(N_i)$ on the basis of some information or data available. Let the available information constitutes the average values :

$$\sum_{\{N_i\}} N_i P(N_i) = \bar{N}_i \qquad (i = 1, 2,...n) \tag{2.3}$$

The probability distribution $P(N_i)$ can then be estimated by the principle of maximum-entropy [6] which consists of maximization of the entropy (2.1) with $W(N_i)$ given by (2.2) subject to the conditions (2.3) and the normalization condition :

$$\sum_{\{N_i\}} P(N_i) = 1. \tag{2.4}$$

The optimization yields the Poisson distribution

$$P(N_i) = \frac{\exp(-\bar{N}_i)(\bar{N}_i)^{N_i}}{N_i!} \tag{2.5}$$

determining the law of probability of the molecular numbers N_i. The probability distribution of $A_n = \{N_1, N_2,..... N_n\}$ according to the ideal gas (or mixture) model of the system, is given by

$$P(A_n) = \prod_{i=1}^{n} P(N_i)$$

or

$$\ln P(A_n) = \ln P(N_1, N_2,..N_n)$$

$$= \sum_{i=1}^{n}\left[N_i - \bar{N}_i - N_i \ln\frac{N_i}{\bar{N}_i}\right. \tag{2.6}$$

Let us now find the thermodynamic significance of the right handside of (2.6). Let $\cup$ be the internal energy, S the entropy, T be the temperature and V be the volume of the system. Then by Gibbs' relation, the change of entropy dS is given by [7] :

$$dS = \frac{1}{T}d\cup + \frac{P}{T}dV - \sum_{i=1}\frac{\mu_i}{T}dN_i, \tag{2.7}$$

where μ_i is the chemical potential of the i-th component The volume V and temperature T being assumed fixed, we have

$$dF = d\cup - TdS = \sum^{n}\mu_i dN_i, \tag{2.8}$$

where $F = d\cup - TS$ is the free-energy of the system.

For the ideal gas model of the system, we have [8]

$$\mu_i = kT\ln\frac{N_i}{\bar{N}_i}, \tag{2.9}$$

where the average $\bar{N}_i$ ($i = 1,2,.....n$) is the statistical equilibrium values of N_i .Putting this value of μ_i in (2.8), we have

$$dF = kT - \sum_{i=1}^{n}\ln\frac{N_i}{\bar{N}_i}dN_i. \tag{2.10}$$

Integrating from the stationary equilibrium state $\{\bar{N}_1, \bar{N}_2 ..... \bar{N}_n\}$ to the non-stationary state $\{N_1, N_2 \quad . N_n\}$, we have

$$F - F_{st} = kT = \sum\left| N_i - N_i - N_i \ln\frac{N_i}{\bar{N}_i}\right. \tag{2.11}$$

which is the expression of free-energy (except an additive constant F_{st}) of the system in terms of the molecular numbers $\{N_1, N_2 ..... N_n\}$ of the different component of species. From eqs. (2.6) and (2.11), we can write the probability distribution of the macrostate $A_n = \{N_1, N_2 ..... N_n\}$ as

$$P(A_n) = P\{N_1, N_2 . \quad . N_n\} \propto e \tag{2.12}$$

wich is well-known result in statistical mechanics [9] and here we have obtained it in an ingenious way in dealing with multi-component thermodynamic system.

3. Multi component system : chemical equilibrium and stability

Let the chemical reaction that occur among the different components be represented by the equation

$$\sum_{i=1}^{n}\upsilon_i B_i = 0, \tag{3.1}$$

where υ_i (i = 1, 2,.....n) are the stochiometric coefficients and B_i (i = 1, 2,.....n) are the chemical symbols of the different substances or components. The molecular number can change as a result of chemical reaction but cannot change arbitarily. They change according to the chemical eq. (3.1). This requires [10]

$$dN_i = \lambda \upsilon_i \ (i = 1,2,.....n), \tag{3.2}$$

where λ is a constant of proportionality. According to Boltzmann and Planck, thermodynamic equilibrium state corresponds to the most probable state of the system subject to given conditions or constants. This requires the maximum value of the probability of the state $P(A_n)$ or equivalently

$$d[\ln P(A_n)] = 0 \tag{3.3}$$

subjected to constraints (3.2). This leads to the equation

$$\sum_{i=1}^{n} \ln \frac{\overline{N}_i}{N_i} dN_i = \lambda \sum_{i=1}^{n} \upsilon_i \ln \frac{\overline{N}_i}{N_i} = 0. \tag{3.3}$$

For ideal gas model of the system for which the chemical potential μ_i is given by (2.9), the condition (3.3) reduces to

$$\sum_{i=1}^{n} \upsilon_i \mu_i = 0 \tag{3.4}$$

From eqs. (2.11) and (3.3), the free-energy change in the reaction is given by

$$dF = -KT \sum_{i=1}^{n} \upsilon_i \left[\ln \overline{N}_i - \ln N_i\right]$$

$$= dF_\circ + kT \sum \upsilon_i \ln N_i \ , \tag{3.5}$$

where $dF_\circ = KT \sum_{i=1}^{n} \upsilon_i \ln \overline{N}_i$ (3.6)

is a quantity (called standard free-energy change of the reaction) depending on T and V, not on the numbers $\{N_1, N_2.....N_n\}$ of molecules present. The equilibrium condition (3.3) then leads to

$$\sum_{i=1}^{n} \ln N_i^{\upsilon_i} = \ln\left(N_1^{\upsilon_1} N_2^{\upsilon_2} .....N_n^{\upsilon_n}\right) = -\frac{dF_\circ}{kT}$$

or $N_1^{\upsilon_1} N_2^{\upsilon_2} .....N_n^{\upsilon_n} = K_N(T,V)$

$$= e^{-dF_\circ/kT} = \overline{N}_1^{\upsilon_1} \overline{N}_2^{\upsilon_2} .....\overline{N}_n^{\upsilon_n} . \tag{3.7}$$

The quantity K_N (T, V) which is independent of the number of molecules $\{N_1, N_2.....N_n\}$ present and depend only on temperature T and volume V of the system, is called the equilibrium constant. The relation (3.7) expressing the relationship among the number of molecules of the different components or species present in chemical equilibrium is known as the law of mass action [10].

Let us now investigate the criteria of stability of the chemical equilibrium state on the basis of the most probable interpretation of the thermodynamic equilibrium state. The condition (3.3) is not sufficient for equilibrium and stability of the system. It must be assumed that the maximum of $P(A_n)$ or equivalently ln $P(A)$ is attained. So the criteria of thermodynamic equilibrium and stability of the system should be stated as

$$\delta[\ln P(A_n) = 0 \Rightarrow \text{crietionof Equilibrium,}] \tag{3.8}$$

$$\delta^2[\ln P(A_n) < 0 \Rightarrow \text{crietionof Stability}] \tag{3.9}$$

Now using (2.9) and (3.4), we have

$$\delta^2 \left[\ln P(A_n)\right] = \delta \left[-\sum_{i=1}^{n} \ln\left(\frac{N_i}{\overline{N}_i}\right) \delta N_i\right]$$

$$= \frac{1}{k} \delta \left[-\sum \ln\left(\frac{\mu_i}{T_i}\right) \delta N_i\right]$$

$$= \frac{1}{k} \sum\sum \frac{\partial}{\partial N_j}\left(\frac{\mu_i}{T_i}\right) \delta N_i \delta N_j \tag{3.10}$$

So the condition of thermodynamic stability becomes

$$-\sum\sum \left(\frac{\partial}{\partial N_j}\left(\frac{\mu_i}{T_i}\right)\right) \delta N_i \delta N_j < 0 \tag{3.11}$$

which is the condition of stability of an equilibrium state when fluctuation in the molecular numbers are considered [7]. In fact, this condition is general and can be applied to fluctuation due to chemical reaction as well.

Assuming the fluctuation

$$\delta N_i = \upsilon_{ji} \xi_j \tag{3.12}$$

in which υ_{ji} are the stochiometric coefficients for several chemical reactions (k = 1, 2) with ξ_j as the degrees of advancement of the reactions, we can reduce the inequality (3.11) to the condition of stability of several chemical reactions as [7].

$$\sum_i \sum_j \frac{1}{T}\left(\frac{\partial A_i}{\partial \xi_j}\right) \partial \xi_i \partial \xi_j < 0 \ , \tag{3.13}$$

where

$$A_i = -\sum \mu_j \upsilon_{ji} \tag{3.14}$$

are the affinities. Thus, a system that is stable to diffusion is also stable to chemical reactions. This is well-known Duhem-Jougheut theorem [11].

4. Conclusion

The paper is an extension of an earlier work [12] which deals with a closed multi-component system. It is an attempt on the formulation of a statistical theory of thermodynamic equilibrium by maximising the probability distribution of the macroscopic state, not by maximising the thermodynamic probablility as is usually done. The maximisation of probability distribution subject to the given constraints, corresponds to the most probable state and thermodynamically this has been shown to be equivalent to the thermodynamic equilibrium state by minimising the free-energy of the system. The above method has been successfully and elegantly applied to a chemically reacting multi-component system to determine the condition of chemical equlibrium, the law of mass action and the criteria of chemicalstability of the system.

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